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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

SCHAEFFER et al

Atty. Ref.: 839-856

Serial No. 09/917,796

Group: Unassigned

Filed: July 31, 2001

Examiner: Unassigned

For: THERMAL BARRIER COATING

\* \* \* \* \*

November 7, 2001

Assistant Commissioner for Patents  
Washington, DC 20231

Sir:

**PRELIMINARY AMENDMENT**

In order to place the above-identified application in better condition for examination, please amend the application as follows:

**IN THE SPECIFICATION**

Replace paragraph 0003 beginning on page 1, with the following rewritten paragraph/s:

In recent years, significant advantages have been achieved by using high temperature alloys in gas turbine systems by incorporating iron, nickel and cobalt-based superalloys in coatings applied to the substrate of key turbine components. The purpose of an effective surface coating is two-fold. First, the coating must form a protective and adherent layer that guards the underlying base material against oxidation, corrosion, and

degradation. Second, the coating should have low thermal conductivity relative to the substrate. As superalloy compositions have become more complex, it has been increasingly difficult to obtain both the higher strength levels that are required (particularly at increased gas turbine operating temperatures) and a satisfactory level of corrosion and oxidation resistance. The trend towards higher gas turbine firing temperatures has made the oxidation, corrosion and degradation problems even more difficult. Thus, despite recent improvements in thermal barrier coatings, a significant need still exists for more effective, less degradable high temperature coatings since most alloy components cannot withstand the long service exposures and repetitive cycles encountered in a typical gas turbine environment.

Replace paragraph 0004 beginning at page 2, with the following rewritten paragraph/s:

Many of the known prior art coatings used for gas turbine components include aluminide, MCrAlY and ceramic components. Typically, ceramic coatings have been used in conjunction with a bond coating formed from an oxidation-resistant alloy such as MCrAlY, where M is iron, cobalt, and/or nickel, or from a diffusion aluminide or platinum aluminide that forms an oxidation-resistant intermetallic. In higher temperature applications, these prior art bond coatings form an oxide layer or "scale" that chemically and mechanically bonds to the ceramic layer to form the final bond coating.

Replace paragraph 0009 beginning on page 5, with the following rewritten paragraph/s:

Despite the recent developments in coatings summarized above, there remains a need in the art for an improved zirconia-based coating that is optimal for use in forming protective coatings on metal alloy components exposed to high temperature environments in gas turbine engine components used for electrical power generation. The need also exists for improved methods of applying such coatings to key turbine components exposed to hostile chemical conditions at high temperatures. That is, a need still exists for improved yttria-stabilized zirconia coatings that have strong chemical and erosion resistance when exposed to very hot exhaust gases, while maintaining a spallation resistance comparable to conventional systems such as those taught by Stecura.

Replace paragraph 0010 beginning on page 5, with the following rewritten paragraph/s:

The present invention meets the above needs by providing a new thermal insulating ceramic layer for use in a thermal barrier coating system on metal alloy components designed for use in a hostile thermal environment. Components that are well-suited for coating are nozzles, buckets, shrouds, airfoils, and other combustion hardware found in the hot gas paths of gas turbine engines. The coatings of the present invention tend to reduce the temperature at the surface of the metal alloy because the thermal conductivity of the coating is an order of magnitude lower than that of the metal substrate. Only a thin layer of ceramic is required to reduce the heat flux to a metal when a thermal gradient exists (5-50 mils). The temperature at the surface of the metal can be up to 400°F lower than the temperature at the surface of the ceramic coating. The ceramic layers are particularly suited to applications where the gas temperature is in

excess of 1000°C and/or where severe thermal cycle fatigue stresses exist due to repeated start ups and shut downs of the gas turbine.

Replace paragraph 0011 beginning on page 6, with the following rewritten paragraph/s:

Surprisingly, it has now been found that an improved thermal insulating ceramic layer in accordance with the invention can be formed of zirconia that has been partially stabilized by yttria in the amount substantially lower than predicted by Stecura, namely about 4 weight% (referred to herein as "4 YSZ"). For the first time, it has also been found that the yttria-stabilized zirconia can be applied using a dense vertically cracked ("DVC") vapor deposition process. Using the DVC process, the yttria transforms the ceramic into a tetragonal crystal structure that resists volume changes during repeated thermal cycling. The stabilized transformation also toughens the zirconia when mechanical stresses are applied. Preferably, the zirconia formed using the DVC process includes 0-1% by weight Hafnia ( $\text{HfO}_2$ ) in solid solution.

Replace paragraph 0016 on page 8:

FIGURE 1 shows a thermal barrier coating in accordance with the invention as applied to a substrate using a DVC technique like thermal spray. The coating 10 includes a thermal-insulating ceramic layer 12 over a bond coating 14 that overlies a metal alloy substrate 16 which typically forms the base material of the turbine blade. Suitable materials for the substrate include iron, nickel, and cobalt-base superalloys. As indicated above, the bond coating must be oxidation resistant and typically forms an alumina layer 18 on the surface of the bond coating when the coated blade is exposed to elevated

temperatures. The alumina layer serves to protect the underlying superalloy substrate 16 from oxidation and provides a surface to which the ceramic layer adheres.

Replace paragraph 0017 beginning on page 8, with the following rewritten paragraph/s:

According to the present invention, the preferred material for the ceramic layer 12 consists of zirconia partially stabilized with about 4 weight% yttria. The zirconia also includes 0-1% Hafnia ( $\text{HfO}_2$ ) in solid solution. The ceramic layer preferably is applied with the dense vertically cracked ("DVC") process such as plasma spray. The yttria transforms the ceramic into a tetragonal crystal structure that effectively resists volume changes during thermal cycling. The stabilized transformation also toughens the zirconia when mechanical stresses are applied to the turbine blade during, for example, startup and shutdown.

Replace paragraph 0018 beginning on page 9, with the following rewritten paragraph/s:

Bond coating 14 is formed from an oxidation-resistant alloy such as  $\text{MCrAlY}$ , where M is iron, cobalt, and/or nickel, or from a diffusion aluminide or platinum aluminide that forms an oxidation-resistant intermetallic. Such bond coatings are well known in the art and typically range in thickness from about 0.002 to about 0.025 inches.

## **IN THE CLAIMS**

1. (Amended) A thermal barrier coating system for use on a metallic component of a gas turbine engine comprising a thermal insulating ceramic layer formed by a dense

vertically cracked vapor deposition process and consisting of about 1 to 5 weight% yttria, 0-1 weight% Hafnia, and the balance zirconia.

8. (Amended) A thermal barrier coating system comprising:

a metallic substrate component of a gas turbine engine;

a thermal insulating ceramic layer of yttria-stabilized zirconia having between 1 and 5 weight percent yttria and about 1 weight percent Hafnia, the thermal insulating layer being deposited by dense vertical cracking; and

a bond coating that adheres the thermal insulating layer to said substrate.

**REMARKS**

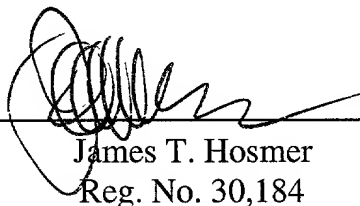
Applicant respectfully requests entry of the foregoing amendments to the specification and claims in order to place the application in better condition for examination. In essence, the suggested changes are typographical in nature and/or represent minor clarifications and corrections to technical terms used in the original specification and claims. As such, applicant submits that the proposed changes do not constitute new matter, particularly since the descriptions of the same constituents and their functionality to the claimed invention appear either explicitly or implicitly in the specification and claims as originally filed.

For the Examiner's convenience, attached hereto is a marked-up version of the changes made to the specification and claims by the current amendment. The attached page is captioned "**Version With Markings To Show Changes Made.**"

Respectfully submitted,

**NIXON & VANDERHYE P.C.**

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**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

**IN THE SPECIFICATION**

Paragraph 0003 beginning on page 1:

In recent years, significant advantages have been achieved by using high temperature alloys in gas turbine systems by incorporating iron, nickel and cobalt-based superalloys in coatings applied to the substrate of key turbine components. The purpose of an effective surface coating is two-fold. First, the coating must form a protective and adherent layer that guards the underlying base material against oxidation, corrosion, and degradation. Second, the coating should have low [thermoconductivity] thermal conductivity relative to the substrate. As superalloy compositions have become more complex, it has been increasingly difficult to obtain both the higher strength levels that are required (particularly at increased gas turbine operating temperatures) and a satisfactory level of corrosion and oxidation resistance. The trend towards higher gas turbine firing temperatures has made the oxidation, corrosion and degradation problems even more difficult. Thus, despite recent improvements in thermal barrier coatings, a significant need still exists for more effective, less degradable high temperature coatings since most alloy components cannot withstand the long service exposures and repetitive cycles encountered in a typical gas turbine environment.

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used in conjunction with a bond coating formed from an oxidation-resistant alloy such as MCrAlY, where M is iron, cobalt, and/or nickel, or from a diffusion aluminide or platinum aluminide that forms an oxidation-resistant intermetallic. In higher temperature applications, these prior art bond coatings form an oxide layer or "scale" that chemically and mechanically bonds to the ceramic layer to form the final bond coating.

Paragraph 0009 beginning on page 5:

Despite the recent developments in coatings summarized above, there remains a need in the art for an improved zirconia-based coating that is optimal for use in forming protective coatings on metal alloy components exposed to high temperature environments in gas turbine engine components used for electrical power generation. The need also exists for improved methods of applying such coatings to key turbine components exposed to hostile chemical conditions at high temperatures. That is, a need still exists for improved yttria-stabilized zirconia coatings that have strong chemical and erosion resistance when exposed to very hot [hydrocarbon ]exhaust gases, while maintaining a spallation resistance comparable to conventional systems such as those taught by Stecura.

Paragraph 0010 beginning on page 5:

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thermal conductivity of the coating is an order of magnitude lower than that of the metal substrate. Only a thin layer of ceramic is required to reduce the heat flux to a metal when a thermal gradient exists (5-[40]50 mils). The temperature at the surface of the metal can be up to 400°F lower than the temperature at the surface of the ceramic coating. The ceramic layers are particularly suited to applications where the gas temperature is in excess of 1000°C and/or where severe thermal cycle fatigue stresses exist due to repeated start ups and shut downs of the gas turbine.

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Paragraph 0018 on page 9:

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